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TMI-2 PYROPHORICITY STUDIES

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ABSTRACT

This report summarizes an extensive literature review and experimental evaluation of the pyrophoric potential of debris and material from within the TMI-2 reactor system. The literature on pyrophoricity recommends educated caution during handling of the TMI-2 core debris because of the presence of zirconium, zirconium alloys, and the potential for some oxidizable zirconium compounds.

Laboratory testing of zirconium-bearing TMI-2 core debris specimens obtained from locations within the reactor vessel show no pyrophoric potential. These data support TMI-2 accident analyses that have concluded that most of the zirconium particulates in the core were oxidized by the high temperature steam environment during the accident. In addition, the presence of other constituents in the core debris effectively dilutes any oxidizable zirconium, thereby rendering sustained propagation of any pyrophoric events unlikely.

Consequently, a reactor defueling scheme has been developed for TMI-2 which acknowledges that, while complete understanding of the zirconium oxidation state is impossible, the safe handling techniques to be used during defueling minimize the concern for any pyrophoric event.

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SUMMARY

GPU Nuclear, assisted by other organizations, investigated the phenomenon of pyrophoricity to evaluate the possibility of pyrophoric reaction during removal of the damaged core from the TMI-2 reactor. A literature review of pyrophoricity (concentrating on the nuclear industry's experiences with zirconium metal) combined with evaluation of the probable high temperature core material reactions that occurred during the TMI-2 accident, indicated that pyrophoric reactions during defueling were unlikely.

A series of ignition tests were performed on samples of core materials obtained from several locations within the TMI-2 reactor vessel and on nonradioactive simulated core debris specimens. In no case did ignition of TMI-2 core samples occur.

These results, coupled with specific defueling procedures designed to prevent pyrophoric reactions, have eliminated pyrophoricity as a significant defueling concern.

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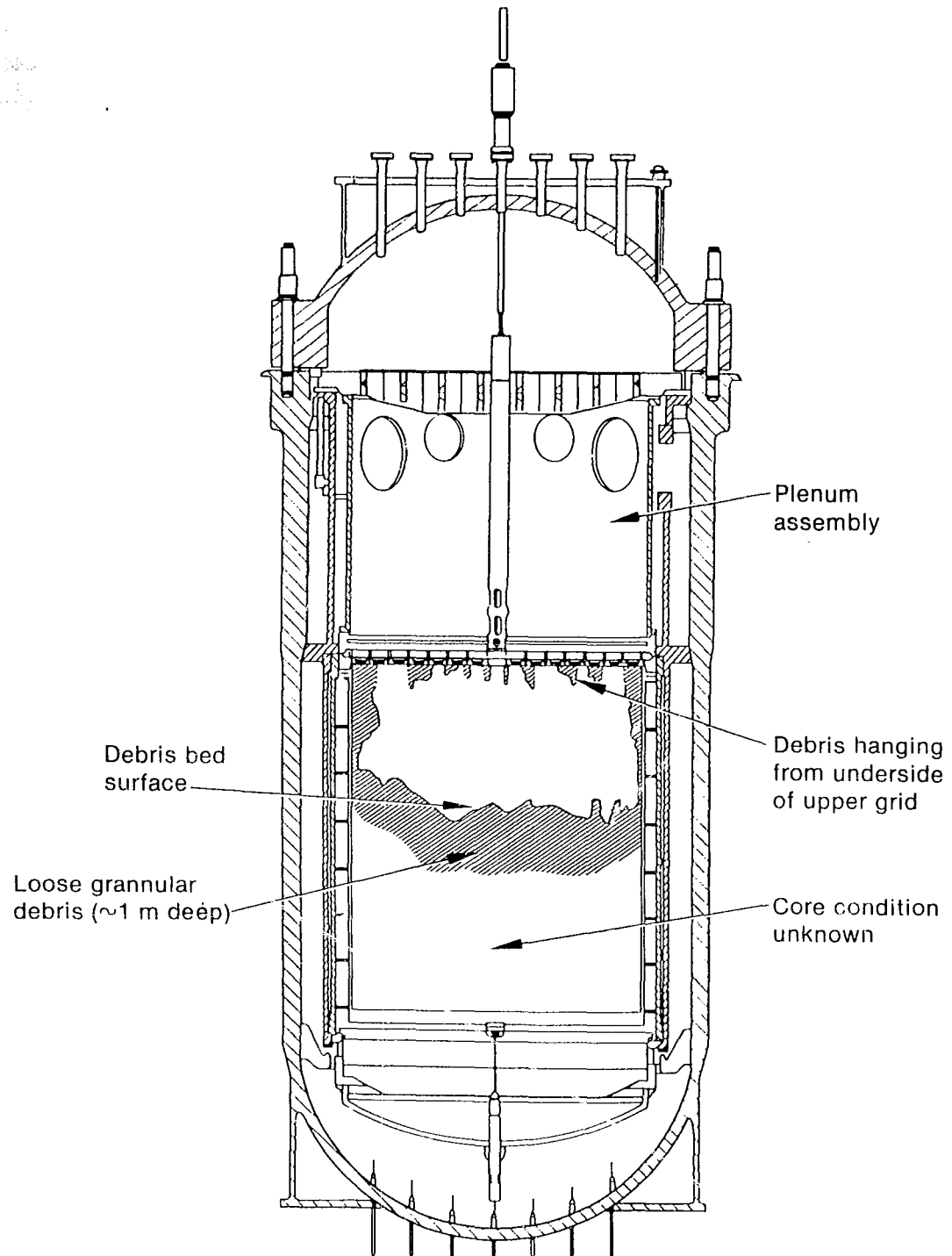
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1. INTRODUCTION

The March 1979 accident at Three Mile Island Unit 2 (TMI-2) produced high fuel temperatures with consequent massive oxidation and fragmentation of the reactor core. The general nature of the core damage was well documented by television camera inspections and core debris sampling. The top part of the TMI-2 core was oxidized and fragmented, leaving an ~1.5-m void at the top of the reactor core. The surface of the remaining rubble bed consists of sand- and gravel-like granular debris with an apparent depth of ~1 m. Regions of once-molten core materials and eutectoid phases (consisting primarily of Zr-U-O) and regions of largely undamaged fuel assembly stubs are believed to underlie this loose debris. The core damage is shown schematically in Figure 1.

It has been suggested that pyrophoric materials might be present within the core debris that could present a safety concern during reactor defueling.¹ The TMI-2 pyrophoricity issue has primarily been concerned with the existence of metals associated with the core debris, which can exist in pyrophoric forms. The principal ceramic materials (i.e., UO_2 , ZrO_2 , etc.) will not support combustion, and hence will not exhibit pyrophoric characteristics. Any metal capable of exothermic reaction with oxygen should, in some state and environment, exhibit a propensity for pyrophoric behavior. The list of metals commonly referred to as combustible metals are those from periodic groups IA, IIA, IIB, IIIB, and IVB (i.e., Li, Na, K, Mg, Ca, Zn, Th, U, Pu, Ti, Zr, and Hf).

The TMI-2 active core region was composed of various ceramics, metals, and alloys, with the principal metallic constituents being Zircaloy-4 (18.8 wt%), control rod alloy Ag-In-Cd (2.2 wt%), stainless steel (1.3 wt%), and Inconel (1.0 wt%) (see Appendix A). The metal of principal interest with respect to pyrophoricity in TMI-2 has been Zircaloy-4, an alloy whose major constituent is zirconium (98 wt%). Other materials whose pyrophoricity should be considered include Zr- UO_2 solids and zirconium hydride thought to have formed from chemical reactions during the accident.



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Figure 1. Schematic of the TMI-2 core damage.

The recovery programs at TMI-2 include head lift, plenum removal, and other operations associated with fuel removal and cleanup of the reactor. These operations, along with reactor defueling and fuel canister handling, will expose new core internals and core debris surfaces. Hence, it can be argued that if any pyrophoric material was created during the accident, these operations would provide the most likely occasion for pyrophoric events. Consequently, an engineering assessment was performed regarding the pyrophoric potential of these operations. The subsequent sections of this report summarize the pertinent literature information and experimental data available from TMI-2 recovery program efforts.

The subject matter covered by the term "pyrophoricity" ranges from mathematical development of combustion theory through concerned opinions regarding unanticipated fires or explosions that have occurred in the agriculture, fuels, and metals industries. The early literature presents a historical record of the state of knowledge at the time of writing, such as the reported occurrences of spontaneous combustion of stored zirconium metal scraps.²

To provide a common basis for understanding the terminology and interpreting both the technical literature and test results, it is necessary to define several terms. A comprehensive and authoritative text on this subject is the Fire Protection Handbook;³ most of the definitions used in this report are taken verbatim from this source.

Pyrophoric Material:⁴ Any liquid or solid that will ignite spontaneously in air below 54.4°C (130°F) is pyrophoric material.

Ignition, Pilot Ignition, and Autoignition:^{3,5} Ignition is the process of initiating self-sustained combustion. If the ignition is caused by the introduction of some small external flame, spark, or glowing object, it is called pilot-ignition. If it occurs without the assistance of an external pilot source, it is called autoignition (also referred to as spontaneous ignition). Studies and experience

indicate that both pilot-ignition and autoignition of solids and liquids are influenced by numerous parameters such as the concentration and flow rate of air, the size and form of the solid or liquid, the concentration and type of impurities in the solid or liquid, the extent of water present, the prior treatment of the solid or liquid, etc.

Ignition Temperature:^{3,5} The ignition temperature of a substance is the minimum temperature to which it must be heated to ignite.

Usually, the pilot-ignition temperature of a substance is considerably lower than its autoignition temperature.

Combustion:³ Combustion is an exothermic self-sustaining reaction involving a fuel (condensed or gas phase) and oxidant.

Chemically, all elements not in their highest oxidation state can undergo oxidation. Consequently, all metals will oxidize in air under appropriate conditions. Given appropriate additional conditions, some metals oxidize rapidly in the presence of air or moisture, generating sufficient heat to reach ignition temperatures. Others oxidize so slowly that heat generated during oxidation is dissipated and ignition temperature is never reached. Certain metals are listed as combustible metals because of their potential for combustion under appropriate conditions--zirconium is included in this classification.

Other terms such as deflagration and detonation are also used in conjunction with combustion. Although these terms are not used in this report, their definitions are included here for clarity and completeness.

Deflagration:³ Deflagration is an exothermic reaction that propagates from burning gases to the unreacted material(s) by conduction, convection, and radiation.

Detonation:³ Detonation is an exothermic reaction characterized by the presence of a shock wave in the material(s) that establishes and maintains the reaction. The principal heating mechanism is one of shock compression; the temperature rise is directly associated with the intensity of the shock wave rather than being determined by thermal conduction.

Additional definitions and general information on the subjects of pyrophoricity and combustion are found in References 3 through 8.

2. PYROPHORICITY STUDIES AT TMI-2

As stated in the "Introduction," the principal element of interest for TMI-2 pyrophoricity potential is zirconium, along with its pertinent compounds and alloys.⁹⁻¹² In addition to zircaloy metal, the principal compounds of zirconium associated with the core debris are most likely ZrO_2 and ZrH_2 (not necessarily stoichiometric) and formations of Zr-U solids from zircaloy- UO_2 fuel chemical reactions. Zirconium oxide, ZrO_2 , is in its maximum oxidation state. Zirconium hydride, ZrH_2 , even if stoichiometric, can thermodynamically undergo oxidation and is potentially reactive.¹³

2.1 Literature Overview

The literature discussing zirconium-uranium solids formation resulting from molten zircaloy in contact with UO_2 fuel¹⁴ has not identified the pyrophoric potential, if any, of these materials. However, since these metals may exhibit pyrophoric characteristics under some conditions (i.e., certain surface-to-volume ratios), engineering assessment suggests educated caution be utilized in testing and handling these materials. Section 3 describes some simple tests conducted to evaluate the pyrophoric potential of these materials.¹⁵⁻¹⁹

Two recent publications providing review and analysis of this general subject matter are authored by H. M. Chung.^{20,21} While significant information is presented in these papers, the pertinent point with regard to metal ignition is that experimental data indicate that zircaloy cladding can act as a sink for hydrogen during high temperature (1200°C) oxidation in either steam or hydrogen-steam environments. An absorption fraction of as much as ~20% of the metal-water reaction-produced hydrogen was reported for the temperature range of 1200 to 1700°C.²⁰ However, H. M. Chung et al. have also reported that the chemical form (zirconium or zirconium hydride) is not the pertinent parameter for material ignition; rather, ignition depends on the standard parameters (i.e., surface-to-volume ratio, oxygen concentrations, moisture content, etc.).²² Chung

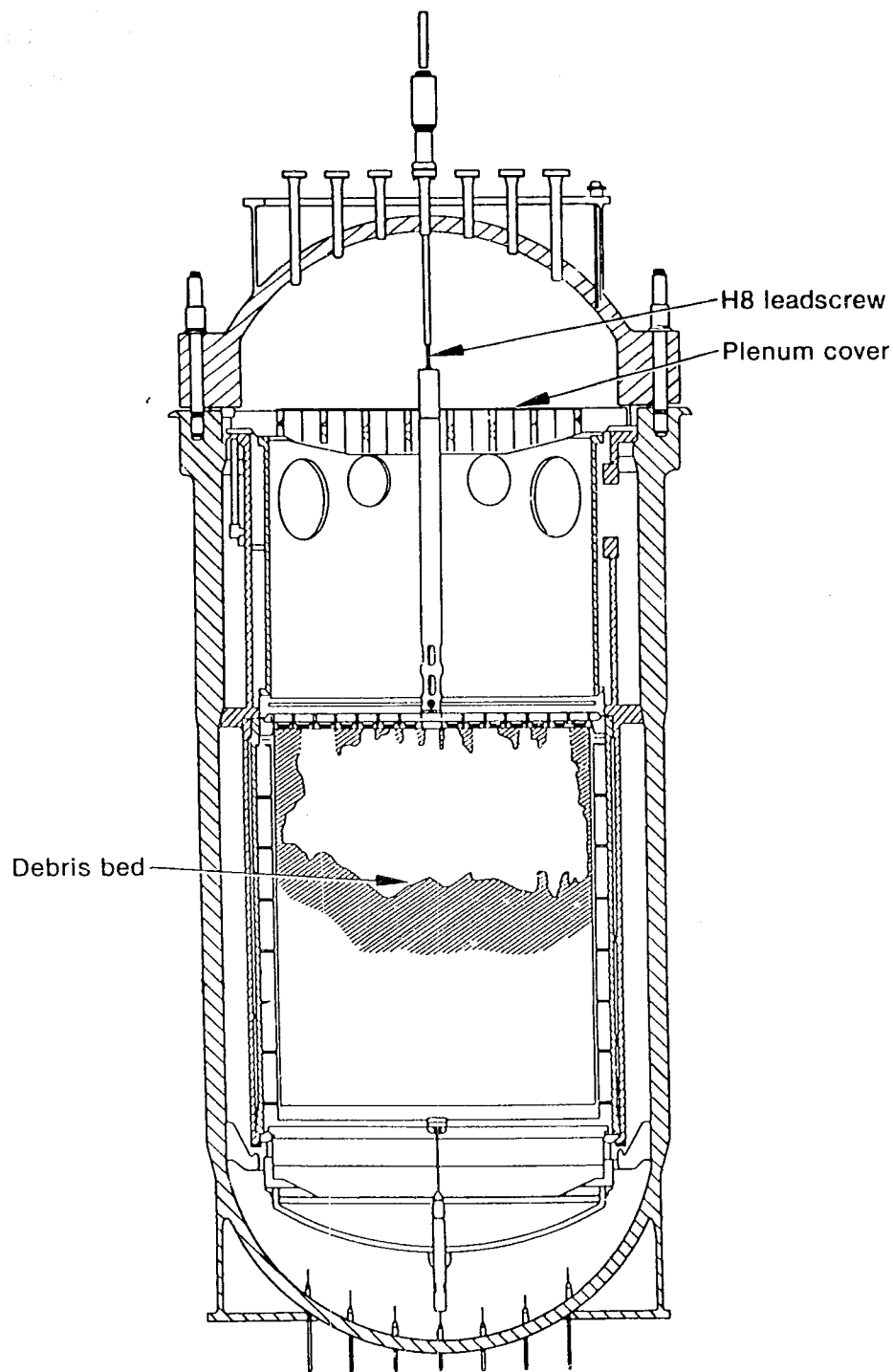
has presented his and Littman's^{15,16} results illustrating autoignition boundaries for sudden exposure of fresh metal surfaces to oxygen-containing atmospheres as a function of metal temperature and oxygen partial pressure; these data are presented in Appendix A.

To quantify the pyrophoric potential associated with the accident-related materials from TMI-2, core debris material was collected from the TMI-2 reactor vessel for experimental evaluation of its pyrophoric characteristics. The following section presents a summary of the type of material collected. Section 3 presents the results of analysis and testing of this material.

2.2 Core Materials Tested for Pyrophoricity

Three types of materials from within the TMI-2 reactor vessel were acquired for chemical analysis and pyrophoric potential evaluation: leadscrew debris deposits, plenum cover debris, and core debris. The general locations from which these specimens were obtained are shown in Figure 2. The TMI-2 leadscrews are ~7-m-long stainless steel rods (threaded over a portion of their length) to which the reactor's control rod assemblies are attached. The threaded surface provided a large surface area for collection of fine particulates generated during the accident. The leadscrew located immediately above the center fuel assembly in TMI-2 (called the H8 leadscrew) was removed from the reactor, and loose debris adhering to the leadscrew was collected for analysis and pyrophoricity testing.

Television camera inspection revealed that a small accumulation of fine particulate debris existed on the plenum cover--the large horizontal surface on the top of the reactor plenum structure (see Figure 2). Presumably, this was accident-generated core debris that was swept high in the vessel by waterflow and subsequently settled onto the plenum cover. Samples of this material were obtained for testing by a vacuum suction device which drew a slurry of reactor water and plenum cover debris into a collection bottle. The slurry was filtered to concentrate the solids for testing.



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Figure 2. General locations of the TMI-2 core debris samples acquired for pyrophoricity testing.

Finally, a number of samples of the gravel-like core debris were acquired from the surface and from beneath the surface of the rubble bed, using a specially designed sampling tool (Figure 3). Specimens were withdrawn into shielded transfer casks and shipped to offsite laboratories for evaluation. The following section describes the evaluation of the pyrophoric potential of these core debris specimens, as well as tests performed on selected nonradioactive materials for comparison.

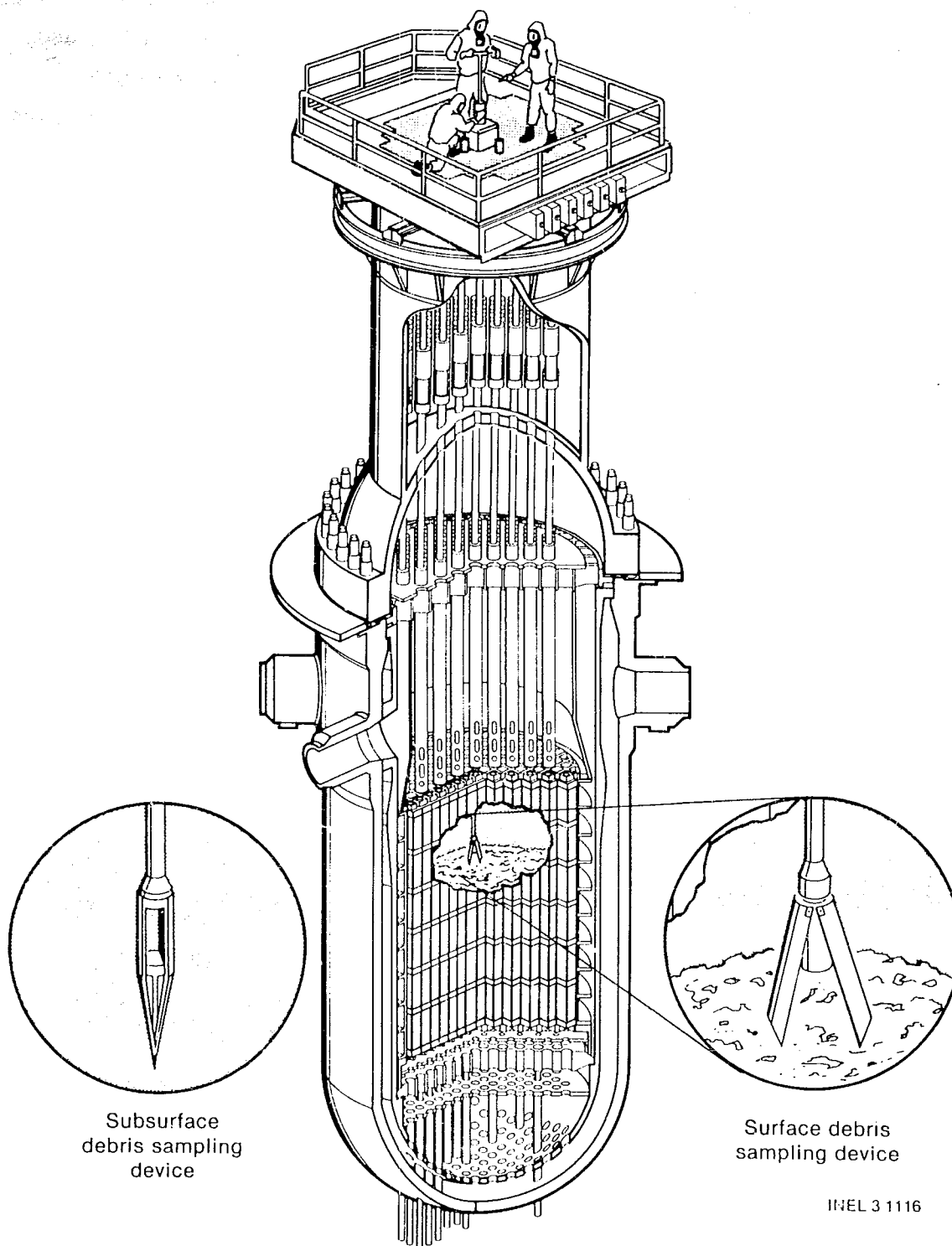


Figure 3. Schematic showing acquisition of the TMI-2 core debris samples.

3. PYROPHORICITY TEST RESULTS

This section describes the results of chemical and physical analyses performed on the core material specimens and laboratory investigations of their pyrophoric and pilot-ignition potential. TMI-2 leadscrew deposits, plenum cover debris, and core debris specimens are discussed in Sections 3.1, 3.2, and 3.3 respectively. In addition, ignition experiments on selected nonradioactive laboratory materials or "standards" (i.e., zirconium, zircaloy, ZrH_2 , iron, etc.) and on a mixture of these "standards" to simulate core debris created by high temperature oxidation are described in Section 3.4

3.1 Leadscrew Deposits

Three sections, each ~30 cm long, were cut from the middle threaded portion of the H8 leadscrew (type 17-4 PH stainless steel) for laboratory examination and analysis. The sections appeared to be in good condition and had a black coating overlaid with heavy rust-colored deposits. The top section was sent to Battelle Pacific Northwest Laboratory (PNL) for analysis,²³ the middle section was sent to the Babcock and Wilcox Company (B&W) Lynchburg Research Center laboratory for analysis,²⁴ and the bottom section was retained onsite for analysis by GPU Nuclear.²⁵ The remaining portion of the H8 leadscrew was sent to the Idaho National Engineering Laboratory (INEL) for analysis.²⁶

The loosely adherent surface deposits on the H8 leadscrew were removed by the various laboratories. Elemental chemical analyses of the metallic constituents of this debris, as reported by the four laboratories, are summarized in Table 1. Variations in the reported values are a result of differences in removal techniques, mass quantities removed, analysis techniques, and the fact that each laboratory received sections from different positions along the length of the leadscrew.

TABLE 1. COMPARISON OF ELEMENTAL CHEMICAL ANALYSES REPORTED FOR THE LOOSELY ADHERENT SURFACE DEPOSITS ON THE H8 LEADSCREW

Element	Reported Metallic Constituents, by Laboratory (wt%)			
	GPU Nuclear	B&W	PNI	INEL
B	NR	0.5	0.7	0.5
Cr	3.8	3.2	0.8	22.0
Fe	33.8	31.5	9.4	37.0
Ni	1.6	1.6	NR	<0.1
Zr	25.4	8.1	7.2	0.4
Mo	4.9	<0.1	0.1	NR
Ag	NR	14.8	NR	<0.1
U	22.8	15.0	NR	ND

NR = Not reported.
ND = Not detected.

PNL provided the most direct information on the pyrophoric potential of the leadscrew deposits by performing differential scanning calorimetry on a specimen of the deposit. This thermal analysis technique determined that the sample did not undergo an exothermic reaction upon heating in air up to ~500°C. The only reportable observation from this analysis was a phase change between 310°C and 450°C.

PNL also performed X-ray diffraction analysis of the leadscrew debris to determine whether any candidate pyrophoric materials were present (i.e., Zr metal, ZrH_2 , etc.). The X-ray diffraction analysis indicated that these phases were not present in detectable quantities. The conclusion reached by PNL was that "chemical and thermal characterizations of the debris thus indicate that the possibility of a pyrophoric process involving the debris from the leadscrew is very small."²³

3.2 Plenum Cover Debris

As part of GPU Nuclear's Underhead Data Acquisition Program, the reactor vessel water level was to be lowered below the plenum cover (see Figure 2), thereby exposing the core material accumulated on the cover to oxygen (air) for the first time. Even though extensive evaluation had indicated no pyrophoric reaction was expected, GPU Nuclear decided to sample and test the plenum cover debris before lowering the water level. Since time did not permit shipment and offsite analysis of the plenum cover sample, a series of tests were developed that were rapid, could be implemented in the limited, onsite radioactive material handling facilities, and were consistent with the generally listed ignition sources for metals. Specifically, the selected tests were the static-charge spark test, an impact test between two surfaces, and a flame pilot-ignition test. The test procedures and sequence were as follows:

1. Spark Test: Place particulate fractions on asbestos board and apply a high voltage spark source from a Tesla coil (10,000-50,000 V, at a frequency of ~0.5 MHz, with an estimated spark energy of 0.2 to 2 MJ); look for visual indication of ignition.

2. **Strike Test:** Observe samples under impact in an enriched oxygen environment. To minimize spread of contamination and provide an enriched oxygen atmosphere, the test procedure involved placing the debris sample fraction in a plastic glove bag containing a small anvil, a hammer, and a small work pad. The test was performed by placing the debris sample fraction on the anvil, partially filling the glove bag with oxygen, sealing the bag, and using the hammer to strike the debris.
3. **Flame Test:** Place a particulate sample fraction on an asbestos board and pass a propane torch flame ($\sim 2300^{\circ}\text{F}$ flame temperature) over the material. This flame test is an extreme pilot-ignition test.

The spark test is the most significant with respect to establishing the pilot-ignition characteristics of the TMI-2 material, because a spark is a common industrial ignition source. The flame test is essentially an extreme test meant to illustrate the complete inertness of the material to ignition or further oxidation. It must be recognized that all these tests are pilot-ignition tests and, therefore, exceed the pyrophoric definition.

The plenum cover sample consisted of a small quantity of reactor coolant water with a few millimeters of fine particulate material on the bottom of the sample container and a reddish-brown suspension above the solids. This liquid and particulate material was filtered through a 0.45- μm millipore filter. The resulting filtered material was dark reddish-brown in color with several metallic silver colored beads. Dose rate readings of 2 R/h gamma and 60 rad/h beta were measured about 10 cm from the sample. The solid sample contained an estimated mass of 20 to 40 mg. The plenum cover sample was subdivided and subjected to two spark tests, one strike test, and two flame tests. The tests were videotaped for documentation. No plenum cover samples exhibited any pilot-ignition.

Following these tests, the reactor water level was lowered below the plenum cover, exposing this entire surface to air. No pyrophoric reactions were observed.

3.3 Core Debris

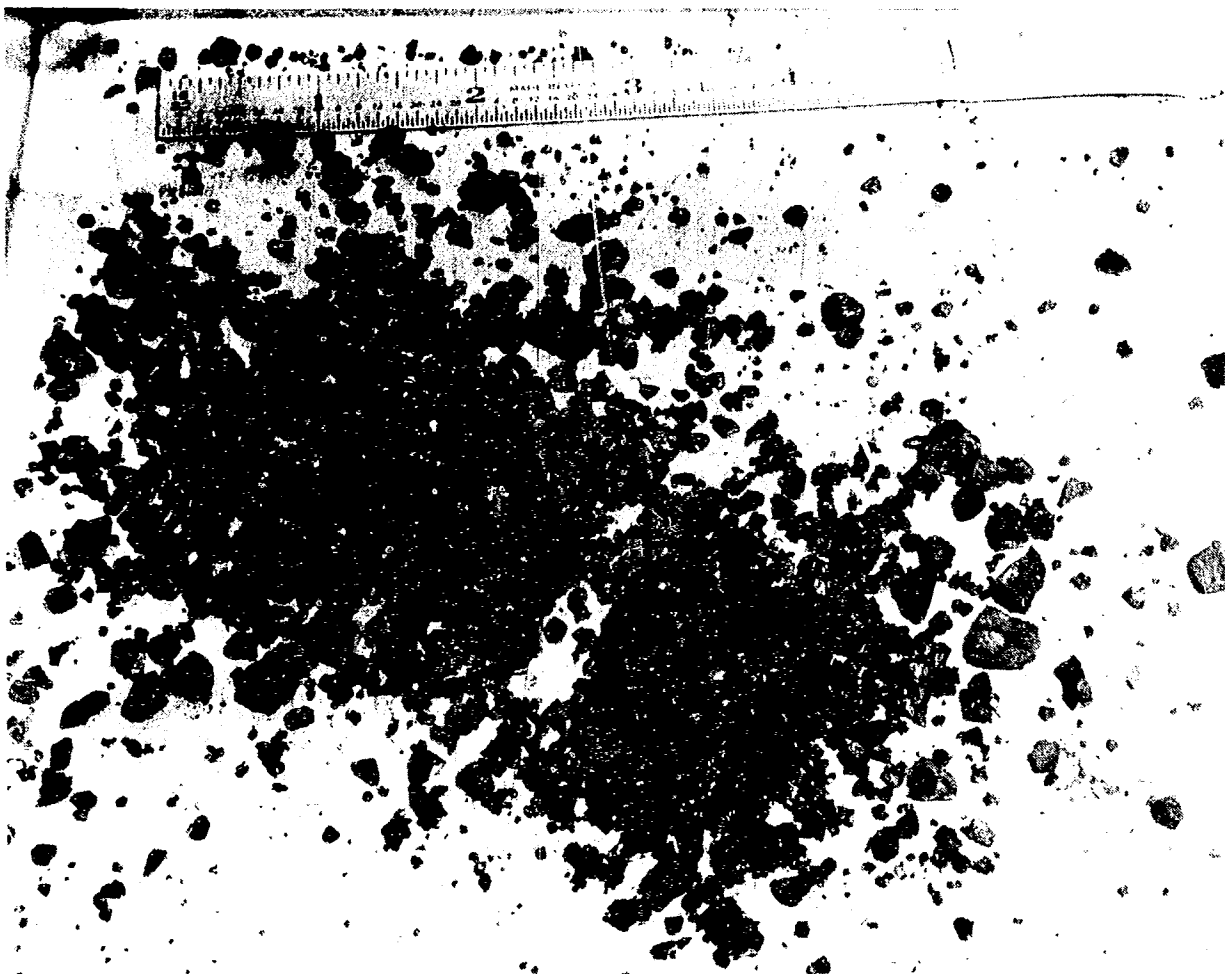
The core debris samples that were selected for pilot-ignition testing were obtained from two core locations at a depth of about 56 cm into the core rubble bed. The two samples, designated H8B and E9B, each consisted of $\sim 30 \text{ cm}^3$ of granular material ($\sim 150 \text{ g}$ each). Figures 4 and 5 illustrate typical core debris samples. Analysis of these samples is still in progress; only limited characterization data are available. The particle size data for the core debris samples are shown in Figure 6.

Initial elemental analysis results from the H8A debris sample (H8A was taken from a depth of $\sim 8 \text{ cm}$ into the debris bed) indicated that the major elements detected were uranium, zirconium, and iron, as presented in Table 2.

Table 2 reports the elemental analyses on the dissolved fraction (the portion of the H8A sample that dissolved during acid dissolution steps) and the undissolved fraction of the H8A sample. Generally, greater than 90 wt% of the H8A sample dissolved; therefore, the dissolved fraction results can be used for assessing the major elements present in the H8A sample.

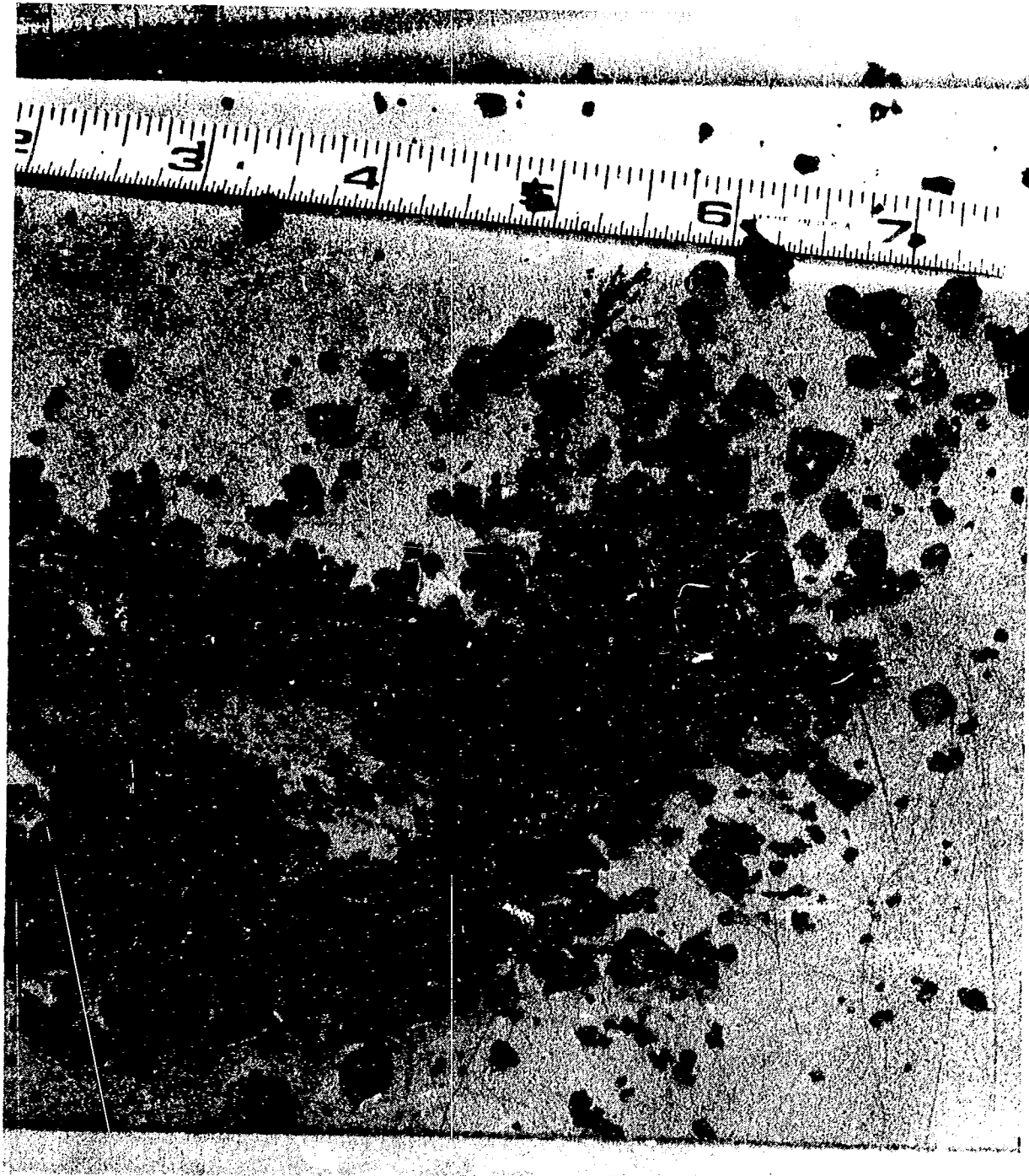
Because the core debris samples are needed for a variety of tests and analyses and because they had been exposed to air following their removal from the reactor vessel, it was decided to limit the pilot-ignition tests to nondestructive Tesla coil spark tests (although two small samples were exposed to a propane torch flame test to confirm their inertness).

The pilot-ignition tests were performed on core debris specimens that had been sieved to produce specific size fractions. The tests concentrated on the larger size fractions because the ignition of debris fines could not



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Figure 4. Photograph of TMI-2 core debris sample H8B.



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Figure 5. Photograph of TMI-2 core debris sample E9B.

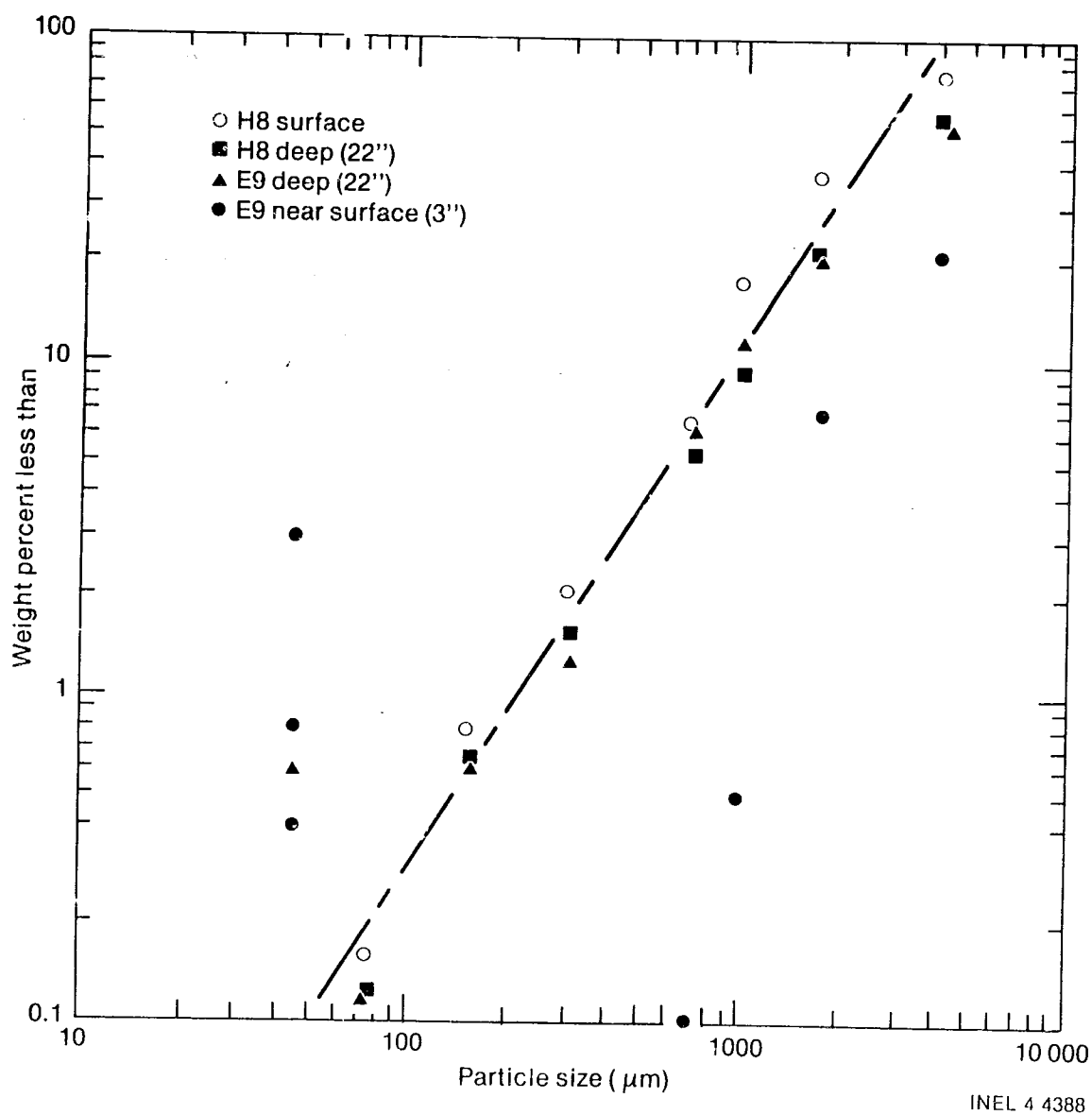


Figure 6. TMI-2 core debris particle size distribution.

TABLE 2. ELEMENTAL ANALYSIS OF CORE DEBRIS SAMPLES

Elemental Analysis of Dissolved Fraction			Elemental Analysis of Undissolved Fraction		
Major ^a	Minor ^b	Trace ^c	Major ^a	Minor ^b	Trace ^c
U	Ni	Sr	Zr	Al	Mn
Zr	Cr	Al	Cr	Ni	Cu
Fe	Ag	In	Fe	Ag	In
			U	Si	B
				Sn	

- a. 10 to 100 wt% of sample.
b. 1 to 10 wt% of sample.
c. <1 wt% of sample.

be construed as a major concern. The basis for this is the known phenomenon of dust ignition by pilot-ignition sources. That is, even innocuous materials (grain dust, iron filings, etc.) of small particle size (generally 250 mesh, 63 μm) can sometimes ignite because of their large surface-to-volume ratios. Figure 6 shows that a very small fraction of the TMI-2 core debris falls into this category. Pilot ignition of larger size particles, however, would be evidence that the core debris could present a safety concern during defueling operations. The specimens were tested both dry and moist, with the definition of moist being ~10-wt% water added to the sample. This value is about mid-range of the 3 to 16-wt% range given as the amount of water that enhances pyrophoricity.¹⁰

Table 3 summarizes the core debris pilot-ignition tests. No pilot-ignition was observed in any of the spark tests, including the smallest particles which might have been expected to ignite simply because of their high surface-to-volume ratios. Figure 7 shows a spark pilot-ignition test.

Two additional pilot-ignition tests, using a flame as a pilot-ignition source, were performed on individual pieces of <4000- μm material from the H8B sample. Both of these pieces weighed less than 1 g. One of the pieces appeared to be a cladding tubing fragment. The other piece appeared to be porous ceramic material. No observed pilot-ignition occurred with either of these particles from the flame tests. Figure 8 shows the flame pilot-ignition test.

The spark and flame pilot-ignition tests confirm the inertness of these core debris samples to pilot-ignition. These tests were videotaped for documentation and interpretation. The videotapes are available for review, upon request to GPU Nuclear.

3.4 Simulated Core Debris

Selected nonradioactive powders were subjected to moist and dry spark and flame ignition tests. These tests were performed and videotaped to provide a frame of reference for comparison with similar tests conducted on

TABLE 3. TMI-2 CORE DEBRIS PILOT-IGNITION TEST RESULTS

Sample	Particle Size Range ^a (μm)								
	<u>>4000</u>	<u><4000</u> <u>>2000</u>	<u><2000</u> <u>>1190</u>	<u><1190</u> <u>>734</u>	<u><734</u> <u>>320</u>	<u><320</u> <u>>149</u>	<u><149</u> <u>>74</u>	<u><74</u> <u>>44</u>	<u><44</u>
H8B (center of the core, ~56 cm into rubble bed)	NI ^b	NI	NI	NI	NI	NI	NI	NR ^c	NR
E9B (half-radius of the core, ~56 cm into rubble bed)	NI	NI	NI	NI	NI	NI	NI	NI	NR

a. Each particle size range was tested both dry and with 10-wt% water added.

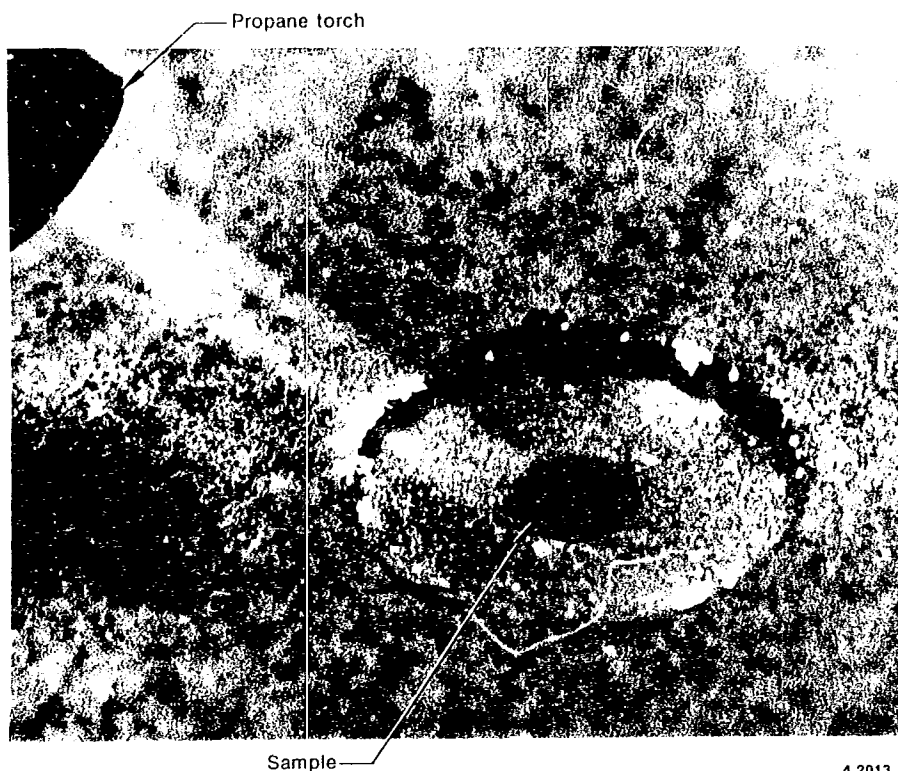
b. NI = no pilot-ignition.

c. NR = sample not run because of insufficient material.



4 2012

Figure 7. Photograph showing a spark pilot-ignition test.



4 2013

Figure 8. Photograph showing a flame pilot-ignition test.

selected core debris as discussed above. These tests also served to demonstrate the validity of the basic test by demonstrating that selected laboratory (reference standard) materials would pilot-ignite as stated.

The following reference powders were evaluated:

Zirconium ($<44\ \mu\text{m}$)

Zircaloy-2 ($>44\ \mu\text{m}$, $<177\ \mu\text{m}$)

Zircaloy-2 hydride ($<48\ \mu\text{m}$)

Zirconium dioxide ($<44\ \mu\text{m}$)

Iron ($<149\ \mu\text{m}$)

Uranium dioxide ($<44\ \mu\text{m}$)

TMI-2 mix (a combination of the above materials).

The standard tests confirmed that selected metallic materials in appropriate physical and chemical form (i.e., Zr powder and ZrH_2 powder) would be pilot-ignited, whereas no significant pilot-ignition and propagation resulted from tests on the TMI-2 mix. Additional information on these tests is provided in Appendix A.

As part of an ongoing program of severe core damage experiments, Oak Ridge National Laboratory (ORNL) has performed a number of small scale ($\sim 1\ \text{kg}$), high temperature core melt experiments. These experiments contained zircaloy cladding, UO_2 pellets, Ag-In-Cd control rod alloy, and stainless steel. This combination of materials and the test conditions (temperatures $>2000^\circ\text{C}$, in steam) makes the experiments particularly relevant to TMI-2. The chemical interactions between zircaloy and UO_2 discussed in the literature can be observed from these ORNL core melt materials. Much of the core melt material had a black, glassy appearance, indicating the evidence of Zr- UO_2 wetting and interaction phenomena. Samples from various test melts were provided by ORNL for a variety of tests, including pilot-ignition tests. The material ranged in size fractions from large pieces to particles from $\sim 1\ \text{cm}$ to $\sim 300\ \mu\text{m}$. Observations and test results on this ORNL core melt material follow.

A glass container of ~250 g of granular (~1-cm) pieces of simulated core material would produce a few sparks when shaken. Pitting of the glass sample bottle indicates the melt material hardness is greater than glass. The pertinent point here is that there was a limited amount of sparking and no sustained ignition. This limited amount of sparking is consistent with the small amount of metallic phase (with a thickness of 1 to 5 μm reported in the literature) being exposed to an oxygen environment.²⁷

Pilot ignition tests were performed by torch heating specimens (to a dull red glow) in flowing air held in a Pyrex apparatus. The specimens consisted of ~35 g of particles ranging in size from ~300 μm to ~5 mm. This test produced a few sparks upon heating but no sustained ignition. TMI-2-type flame tests on individual large particles (several millimetres in size) also were conducted. These tests produced no sparks or ignition; some particles fractured, presumably from thermal stresses.

4. CONCLUSIONS AND COMMENTS ON TMI-2 REACTOR DEFUELING

The general recommendation from a review of the literature is that educated caution must be used in handling potentially combustible metallics such as zirconium-bearing materials. Chemical analyses and pilot-ignition tests on a variety of accident-generated materials (leadscrew deposits, plenum cover debris, and core rubble bed debris) indicated absolutely no tendency toward pyrophoricity or pilot-ignition. Other observations made during the course of recovery activities (i.e., exposure of the entire plenum cover to air, exposure of bulk core debris samples to air during shipping, handling in air of leadscrews containing surface deposits of particulate debris) also indicated no pyrophoricity of core debris. During tests conducted on simulated core material, sparking was observed from isolated particle surfaces, but no bulk pilot-ignition or sustained propagation was observed.

These observations would indicate that reactor bulk defueling can proceed without extraordinary procedures for handling pyrophoric material. Other factors inherent in the defueling process itself further reduce any pyrophoric hazard. These factors include the following:

- Defueling will be conducted at ambient temperatures; extreme sources of ignition (i.e., cutting torches) are not planned for use
- Oxidized debris and oxidized core materials will act as a dilutant to any pyrophoric materials
- Defueling will occur underwater, and the large amount of water will act as a heat sink for any material temperature rises that occur during defueling.

It is the opinion of the authors that there is minimum concern for a pyrophoric event or sustained propagation during underwater defueling of the TMI-2 reactor vessel. A recent evaluation by the U.S. Nuclear

Regulatory Commission of the TMI-2 pyrophoricity hazard²⁸ also reached this conclusion. It is possible that surface oxidation of freshly exposed metallic surfaces could occur during defueling and that such oxidation would generate hydrogen gas from radiolytic decomposition of water from wet fuel debris; data indicate this probability is low. Hydrogen gas accumulations are a potential concern; therefore, evaluations should ascertain the hydrogen accumulations and eliminate them, if necessary, through engineering controls (i.e. venting, controlled combustion, absorption, or other engineered safety features).

The U-Zr alloy material and fuel rod stubs represent a potential concentration of partially oxidized metallic zirconium. Accordingly, the authors recommend that the following additional studies be performed:

1. Pilot-ignition tests and chemical analyses on positively identified specimens of alloy material obtained from existing or future core debris samples
2. Pilot-ignition tests on positively identified specimens of partially oxidized zircaloy cladding (from rod stub assemblies or fragmented fuel rod cladding pieces) obtained from existing or future core debris samples.

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